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(54) PRODUCTION METHOD FOR ULTRAFINE-CELL FOAM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for producing an ultrafine-cell foam without the necessity for a high-cost equipment, such as a pressure tank, and without requiring long time for gas dissolution.
SOLUTION: This method produces an ultrafine-cell foam by using a foam production apparatus which is equipped with a plurality of pumping means for metering and delivering raw material components necessary for producing a polyurethane or polyisocyanurate foam, a plurality of transport means for transporting the raw material components delivered by the pumping means to the objective site, and a mixing chamber for mixing the raw material components. The method is characterized in that the pressure of at least one raw material component flowing through the transport means is set at 20 × 102 kPa or higher and that a gas is continuously dissolved into the raw material component flowing through the transport means under a pressure higher than that of the component.

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CLAIMS

[Claim(s)]
[Claim 1] While setting the raw material component pressure of at least 1 component which is the method of overly manufacturing detailed foam form, and flows the inside of the aforementioned transportation means using a form manufacturing installation characterized by providing the following as 20x102 or more kPas it is characterized by dissolving gas in the raw material component in the aforementioned transportation means continuously by the pressure higher than the raw material component pressure which flows the inside of this transportation means -- super- -- the manufacture method of detailed foam form Two or more pump meanses which measure and carry out the regurgitation of two or more raw material components required to manufacture a polyurethane foam or a polyisocyanurate foam. Two or more transportation meanses to convey the raw material component breathed out from the aforementioned pump means to the target place. A mixing chamber means to mix two or more of said raw material components.
[Claim 2] The manufacture method according to claim 1 which is characterized by what the raw material component pressure of at least 1 component which flows the inside of the aforementioned transportation means is set as 40x102 or more kPas for and which is overly detailed foam form.
[Claim 3] Claim [which is characterized by using a stood / still / type gas dissolution machine in order to dissolve gas in the raw material component which flows the inside of the aforementioned transportation means] 1, or claim 2 publication is overly the manufacture method of detailed foam form.

[Claim 4] the claim 1 which dissolves CO2 gas constituents in the raw material component which flows the inside of a transportation means by which were poured into the raw material component which flows the inside of a transportation means above the critical pressure while the aforementioned gas was CO2 gas, and the raw material component pressure of at least 1 component was set as at least 70x102 or more kPas, or 3 -- either -- a publication -- super- -- the manufacture method of detailed foam form

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the method of overly manufacturing detailed foam form, about methods overly of manufacturing detailed foam form, such as a polyurethane foam or a polyisocyanurate foam, by pouring in gas under specific conditions in the transport process of a raw material component in more detail.
[0002]
[Description of the Prior Art] Conventionally, the polyurethane foam or the polyisocyanurate foam is manufactured using the facility generally called foaming machine. This equipment consists of a mixing chamber (mixing chamber) which mainly mixes two or more raw material components with two or more tanks and two or more pumps, raw material transportation piping which connects the aforementioned tank and a pump, and transportation piping which connects a mixing chamber with the aforementioned pump.
[0003] Moreover, although a polyurethane foam or a polyisocyanurate foam is generally manufactured considering a polyol, the poly isocyanate, a foam stabilizer, a catalyst, and a foaming agent as an indispensable component, it divides these raw materials into two or more components if needed, and is manufactured with the facility called the above-mentioned foaming machine. In this case, if it mixes, two or more components which cause a reaction will be divided, two or more tanks will be filled up, and a mixing chamber is injected and mixed through each tank, a pump means, and a transportation means.
[0004] By the way, the manufacture method of dissolving gas and making the form of a detailed foam forming into each raw material component is well-known so that it may become supersaturation in the flow and pressure requirement of a mixing chamber in the aforementioned foaming machine. By applying more high-pressure air or N2 gas, for example in 1 each raw material component tank as a concrete method The method of making the gas in a raw material component a supersaturation state by the mixing chamber etc. is mentioned by decompressing the pressure of the method of dissolving more gas, the method of pouring in gas compulsorily into 2 raw-material transportation piping, and dissolving or distributing, and three mixing chambers below to an ordinary pressure.
[0005] Although these solution gases are extremely few amounts compared with CO2 capacity produced by the reaction of the water and the isocyanate component which are a foaming agent, it is poured in in order to generate more cellular nuclei and to generate detailed foam form, since fluid pressure declines rapidly by the mixing chamber.
[0006] The gas produced on the other hand by boil of the CO2 gas or the organic solvent generated at the reaction of an isocyanate and water is gas which occurs serially, and in order to carry out only the work which is spread in the cellular nucleus already generated, without making a cellular, almost new nucleus generate, and enlarges the foam, a solution gas differs in work.
[0007] Conventionally, the method of putting a high pressure by the raw material component tank, and forming detailed air bubbles is indicated by JP,61-3663,B (the conventional technology 1), JP,10-58462,A (the conventional technology 2), and JP,59-10915,A.

[0008] (1) Make reactant mixture flow from a single die input, and completing the extruding die which does not make the interior of a die divide or more into two substantially is indicated that the fault which produces from using the extruding die which changes to the conventional technology 1 from the aggregate of the small die which has the die side which is easy generating the fault and the gel by dividing reactant mixture into two or more paths in flowing into an extruding die in a center section should remove. However, cellular structure of 100 micrometers or less / KE called microcell cannot be made to generate by several kg tank pressure (pressure of the gas to pour in) shown in the conventional technology 1.

[0009] (2) these 2 after saturating each component in two airtight containers with gas on the conventional technology 2 component -- mixing -- this mixture -- metal mold -- making it react, changing a pressure and/or temperature inside, and manufacturing foaming synthetic resin is indicated Here, although putting a pressure on an airtight container 60 to 80x102 kPa is indicated and a detailed foam can be realized in this case, while a tankage becomes expensive, in order to fully saturate gas in an airtight container, there is a fault which requires a long time.

[0010] (3) Only pouring in air and N2 gas into transportation piping of a polyol component is indicated by the conventional technology 3. However, this method is general technology currently performed in manufacture of general block form, and it is the limit which is made about (about 150micrometers/ (piece)) a maximum of 50% of cellular size by this method to the form which does not pour in gas at most. In addition, although there is also the method of using together the stirrer other than the above-mentioned technology, and making the dissolution quick, this method as well as the conventional technology 3 has a problem in cellular size.

[0011] Moreover, not only an installation cost is expensive, but the method of changing more into a supersaturation state the solution gas in the raw material component which is made to decompress the pressure of a mixing chamber below to an ordinary pressure, and is injected by the mixing chamber has the fault to which cellular size does not become small extremely, either.

[0012]

[Problem(s) to be Solved by the Invention] It aims at the thing which can overly manufacture detailed foam form continuously for a long time, without also needing a mass tank and for which the manufacture method of detailed foam form is overly offered, without using a reduced pressure mixing chamber facility, without the dissolution of gas taking a long time, while this invention was not made in consideration of the above-mentioned situation and does not need a facility of an expensive proof-pressure tank etc.

[0013]

[Means for Solving the Problem] this invention two or more raw material components required to manufacture a polyurethane foam or a polyisocyanurate foam Measurement and two or more pump meanses which carry out the regurgitation, Two or more transportation meanses to convey the raw material component breathed out from the aforementioned pump means to the target place, The form manufacturing installation possessing a mixing chamber means to mix two or more of said raw material components is used. While setting up the raw material component pressure of at least 1 component which is the method of overly manufacturing detailed foam form, and flows the inside of the aforementioned transportation means more than 20x102kPa (20kg/cm2) it is characterized by dissolving gas in the raw material component in the aforementioned transportation means continuously by the pressure higher than the raw material component pressure which flows the inside of this transportation means -- it is overly the manufacture method of detailed foam form

[0014]

[Embodiments of the Invention] Hereafter, it explains in more detail about this invention.

[0015] In this invention, a raw material component pressure is set as 20x102 or more kPas because the detailed air-bubbles generation effect is small in less than 20x102 kPas. Moreover, as for a raw material component pressure, it is desirable to make it 40x102 or more kPas, and it is still more desirable to make it especially 60x102 or more kPas.

[0016] In this invention, you may pour in continuously the gas injected into a raw material component

directly through capillary tubes, such as glass or a metal, inorganic, or an organic open-cell object into the raw material component in piping as a transportation means. By the aforementioned method, although it is difficult, by enlarging distance from pouring to a mixing chamber, and setting up the dissolution time of gas greatly, making it dissolve into a raw material component in large quantities can dissolve a lot of gas into a raw material component, and it can enlarge the detailed air-bubbles effect. Here, as a method of pouring in gas effectively in a raw material component, it is good to make a dynamic mixer or a stood [still] type mixer distribute rather than to only to pour in gas, and to dissolve a lot of gas for a short time into a raw material component. Especially, as a desirable mixer, it is a stood [still] type mixer, and there is no leakage of the fluid from the axis of rotation by the pressure of a high-pressure fluid like a dynamic mixer. Moreover, ultrasonic stirring can be used similarly independently.

[0017] Although there are for example, a screw type and a pin type type as the aforementioned dynamic mixer and there is a method which put the glass bead in the pipe in addition to the screw type which twisted 180 degrees of rectangular boards to the right-and-left opposite direction as the aforementioned stood [still] type mixer, and the pin type type, when a raw material component is a hypoviscosity liquid and a glass-bead method and a raw material component are hyperviscous liquids, a screw type is desirable at the small point of pressure loss.

[0018] In this invention, as gas which injects the inside of a transportation means into the flowing raw material component, although air, N2 gas, argon gas, gaseous helium, CO2 gas, etc. are mentioned, for example, especially CO2 gas is desirable.

[0019] In this invention, in order not to take the method which a high pressure gas is enclosed [method] with a high-pressure endurance tank over a long time, and dissolves a lot of gas into a raw material component but to dissolve gas for a short time in the transportation means process between a pump means and a mixing chamber means, CO2 gas which is easy to dissolve in a polyurethane-foam raw material or a polyisocyanurate-foam raw material is desirable. Although in the case of CO2 gas a cellular detailed-ized effect is large even if it uses it with 20x102 or more kPas and below critical pressure When it mixes into the raw material component which flows especially by the pressure more than critical pressure at 70x102 or more kPas of a transportation means In the form of kg [25-100]/m3, the diameter of a foam sets in about dozens ofmicrometers/piece, density sets in the form of 300 - 700 kg/m3, and density becomes possible [the thing whose diameter of a foam is about severalmicrometers/piece and for which detailed foam form is overly manufactured].

[0020] by the way, although the technology (latter) of pouring in CO2 gaseous gas into the technology (former) which injects liquefied CO2 into a mixing chamber, and foams to it, or a mixing chamber is in the technology called carbon-dioxide-gas foaming completely apart from this, it should be clearly distinguished from the technology which is this invention CO2 gas which occurs from CO2 of a liquid in the cellular nucleus mainly generated already diffuses the former, using liquefaction CO 2 as a foaming agent, and it grows up a cellular nucleus. Therefore, although air bubbles do not become small but air bubbles become a little large, it is the technology of manufacturing a low density polyurethane foam or a polyisocyanurate foam, without using a chlorofluocarbon system and a non-chlorofluocarbon system solvent. The latter is technology which is made to distribute CO2 gas uniformly and equalizes the permeability of the whole form rather than work of mainly carrying out differential powder of the CO2 gas by stirring by the mixing chamber, and making the diameter of air bubbles small.

[0021] By reducing rapidly the pressure of the raw material which is dissolved in large quantities and conveyed by the high-pressure force in a mixing chamber into a raw material component, CO2 gas of this invention is the point that you are going to generate a cellular nucleus in large quantities in an instant, and are going to make it overly form a detailed foam, and is technology completely different from the above-mentioned carbon-dioxide-gas foaming.

[0022] In this invention, although the position which pours in gas is in the raw material component in a raw material transportation means, it is in the middle of piping which specifically connects a mixing chamber to a pump. However, although it is possible to pour in gas in the middle of the portion which carries out a pump action, and the portion which carries out a mixing chamber operation when the pump and the mixing chamber are unifying as a special example, this method is also included in the range of

this invention.
[0023] In this invention, although it is used for the general-purpose polyurethane foam as the aforementioned pump means and a gear pump, a bosh pump, etc. are easy to be, in order to send a raw material component to a mixed container by the high-pressure force, a bosh pump is desirable. In the case of a gear pump, the sending pressure of a raw material component is used by about 3x102kPa-60x102kPa, and, in the case of a bosh pump, 30x102kPa-150x102kPa is the use range of a general target.
[0024] Although the mixing chamber used may consist of mere loculus which do not build in the case where the mixer which rotates mechanically is built in, and a mixer in this invention, this does not need to build in a mixer with regards to the size of the pressure of the raw material component injected by the mixing chamber, when it is the raw material pressure which is like [with which the raw material generally injected can be mixed enough].
[0025] Although this invention pours in gas into the raw material component sent from a pump, it is effective to pour into a component with much amount used among two or more components of a polyurethane-foam raw material or a polyisocyanurate-foam raw material generally. That is, even if it pours in into a polyol component or the poly isocyanate component and pours in into minor constituents, such as a foaming agent and a foam stabilizer, there are few effects.
[0026] A special raw material does not need to be used for the polyurethane-foam raw material or polyisocyanurate-foam raw material used for this invention, and it can overly manufacture detailed foam form by in addition to this adding a plasticizer, a bulking agent, a stabilizer, etc. if needed by using a general-purpose polyol, the poly isocyanate, a foam stabilizer, a catalyst, and a foaming agent as an indispensable component.
[0027] In this invention, generally it is used and a polyether system polyol, a polyester system polyol, a polydien system polyol, and a polycarbonate system polyol are easy to be as a typical kind as a polyol used. The numbers of functional groups are two or more things, and a thing typical as a polyether polyol has a thing, a polyoxy tetramethylene glycol, etc. which carried out the addition polymerization of polyethylene and the polypropylene to the polypropylene glycol, the polyethylene glycol, and the glycerol.
[0028] A thing typical as a polyester polyol has a polyester polyol, a poly lactone polyol, etc. which are made to condense acids, such as low-molecular-weight polyols, such as ethylene glycol and a diethylene glycol, and a dicarboxylic acid, and have an end OH basis.
[0029] In this invention, as a poly isocyanate to be used, generally it is used and an aromatic poly isocyanate, aliphatic isocyanate, and alicycle group isocyanate etc. is mentioned. Especially the desirable poly isocyanate is an aromatic isocyanate, and has 4 and 4' diphenylmethane diisocyanate, a crude polymethylene polyphenylene poly isocyanate, 2, and 4 tolylene diisocyanate and/or 2, and 6 tolylene diisocyanate as a typical thing, for example. Moreover, the denaturation object of these isocyanates, for example, aloha shirt NETO denaturation, buret denaturation, or a cull BOJIMIDO denaturation object is usable similarly.
[0030] In this invention, the foam stabilizer used is easy to be a commercial thing, and surfactants, such as a polysiloxane-polyoxy-alkylene-glycol copolymer or a sulfonate-ized castor bean oil, are used as a typical thing. Moreover, in the case of a polyurethane foam, it is used for the usual urethane foam and organic-metal catalysts, such as the third class amines, such as a triethylenediamine and a morpholine, or stannous octoate, and dibutyltin dilaurate, etc. are easy to be used as a catalyst. Moreover, in the case of a polyisocyanurate foam, after making a NCO/OH index or more into 1.1 generally, generally, a well-known isocyanurate catalyst is usable. For example, quarternary ammonium salt, an organic-acid alkali-metal salt, etc. are used. Potassium acetate, sodium acetate, N, N', N"-tris (3-dimethylamino propyl) hexahydro-s-triazine, etc. are especially specifically common.
[0031] In this invention, low-boiling point liquids, such as water [which reacts with an isocyanate and generates CO2 gas as a foaming agent used], pentane, hexane, cyclohexane, dichloromethane, 1, and 1-dichloro-1-fluoro ethane, can be used.
[0032] In this invention, although it is possible, and a polyol component is lost as a foaming method

used by any foaming methods, such as an one-shot process, the prepolymer method, and the KUWAJI prepolymer method, in order to make a polyol and the poly isocyanate especially react beforehand by the prepolymer method and to consider as the prepolymer of an end NCO basis, pouring of gas may be limited to a prepolymer in this case.

[0033] In this invention, all flexible polyurethane foams generally called aforementioned polyurethane foam, half-rigid polyurethane foams, and rigid urethane foams are included. Moreover, with a polyisocyanurate foam, half-hard isocyanurate form and all hard isocyanurate forms are included. Furthermore, when it sees from the field of a manufacturing facility, all well-known manufacture methods, such as a slab form manufacture method, a mould form manufacture method, a spray form manufacture method, a sandwiches form manufacture method, and a RIM foaming method, are contained in the range of this invention.

[0034]

[Example] hereafter, one example of this invention is started -- the manufacture method of detailed air-bubbles form is overly explained In addition, a numeric value, material, etc. which are stated in the following example do not show an example, and do not specify this invention. First, the equipment which overly manufactures detailed air-bubbles form is explained with reference to drawing 1 . **** 1 in drawing shows the poly isocyanate component tank (it is hereafter called the 1st tank) which held the poly isocyanate component 2. N2 chemical cylinder 4 is connected to the upper part of this 1st tank 1 through the N2 gas piping 3. It connects with the mixing chamber 8 through the piping 7 which infixed the bosh high pressure pumping (pump means) 5 and the stood [still] type mixer 6 in the bottom of the 1st tank 1 of the above. the aforementioned poly isocyanate component 2 should be measured and breathed out by the aforementioned high pressure pumping 5 here, and pass piping (transportation means) 7 -- it is breathed out by the aforementioned mixing chamber 8

[0035] Liquefaction CO2 bomb 11 is connected to the aforementioned stood [still] type mixer 6 through the carbon-dioxide-gas piping 10 which infixed the mass-flow meter 9 with a flow control. CO2 gas is poured into the stood [still] type mixer 6 for CO2 gas by the mass-flow meter 9 through the carbon-dioxide-gas piping 10 from this liquefaction CO2 bomb 11, and the diffusion dissolution of the CO2 gas is carried out at a raw material component. In the aforementioned mixing chamber 8, the moving vane 13 rotated by the stirring motor 12 is arranged. Here, the mixing chamber means is constituted by the aforementioned mixing chamber 8, the stirring motor 12, and the moving vane 13.

[0036] The polyol component tank (it is hereafter called the 2nd tank) 15 which held a foam stabilizer besides a polyol component, a catalyst, and the mixture 14 that blended the foaming agent suitably is connected to the aforementioned mixing chamber 8 through piping 16. Here, the gear pump (pump means) 17 is infixed in the aforementioned piping 16. A polyol component is measured and breathed out by this gear pump 17, and it is injected by the aforementioned mixing chamber 8 through piping 16, it is breathed out from a mixing chamber 8, reacts with the poly isocyanate, and becomes form. Moreover, N2 chemical cylinder 19 is connected to the upper part of the 2nd tank 15 of the above through the N2 gas piping 18.

[0037] Next, the case where detailed foam form is overly manufactured using the equipment of such composition is explained. While sending the poly isocyanate component 2 through piping 7 from the 1st tank 1, the polyol component 14 is sent to the aforementioned mixing chamber 8 through piping 16 from the 2nd tank 15. Under the present circumstances, the bosh high pressure pumping 5 is infixed in the aforementioned piping 7, while setting the pressure of the poly isocyanate component 2 which flows piping 7 as 50x102 or more kPas, the stood [still] type mixer 6 is infixed in piping 7, and a lot of CO2 gas is dissolved for a short time by high-pressure 60x102kPa rather than the pressure of an isocyanate component. On the other hand, the gear pump 17 was infixed in the aforementioned piping 16, and the pressure of the polyol component 14 which flows piping 16 is set as 10x102 or more kPas.

[0038] Thus, while making high the pressure of the poly isocyanate component 2 which flows under the piping 7 as a transportation means by the bosh high pressure pumping 5 in the above-mentioned example By injecting CO2 gas into the poly isocyanate component 2 in piping 7 in large quantities, making it dissolve in it from liquefaction CO2 bomb 11, and decompressing to an ordinary pressure to

rapid decrease by the mixing chamber 8 More cellular nuclei are generated and the thing of severalmicrometers/piece - about 10micrometers/piece of numbers for which detailed foam form is overly formed can be performed. The raw material pressure which flows under piping 7 especially can be heightened, the gas poured in very much for a short time by pouring in by the gas of the critical pressure can be dissolved, by using together the stood [still] type mixer 6 further, a lot of [further more] gas for a short time can be dissolved in a raw material component, and cellular form overly detailed as a result can be manufactured.

[0039]

[Effect of the Invention] The manufacture method of detailed foam form can overly be offered that detailed foam form can be manufactured continuously for a long time, without also needing a mass tank, without using a reduced pressure mixing chamber facility according to this invention, without the dissolution of gas taking a long time, while not needing a facility of an expensive proof-pressure tank etc., as explained in full detail above. Moreover, while the more flexible form in a soft foam became possible by overly considering as a detailed foam, in the rigid foam, the form of low-fever conductivity became possible and manufacture of the form which changes sharply [a property] with capacity in which the same raw material combination is also dissolved was attained.

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the method of overly manufacturing detailed air-bubbles form, about methods overly of manufacturing detailed air-bubbles form, such as a polyurethane foam or a polyisocyanurate foam, by pouring in gas under specific conditions in the transport process of a raw material component in more detail.

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PRIOR ART

[Description of the Prior Art] Conventionally, the polyurethane foam or the polyisocyanurate foam is manufactured using the facility generally called foaming machine. This equipment consists of a mixing chamber (mixing chamber) which mainly mixes two or more raw material components with two or more tanks and two or more pumps, raw material transportation piping which connects the aforementioned tank and a pump, and transportation piping which connects a mixing chamber with the aforementioned pump.

[0003] Moreover, although a polyurethane foam or a polyisocyanurate foam is generally manufactured considering a polyol, the poly isocyanate, a foam stabilizer, a catalyst, and a foaming agent as an indispensable component, it divides these raw materials into two or more components if needed, and is manufactured with the facility called the above-mentioned foaming machine. In this case, if it mixes, two or more components which cause a reaction will be divided, two or more tanks will be filled up, and a mixing chamber is injected and mixed through each tank, a pump means, and a transportation means.

[0004] By the way, the manufacture method of dissolving gas and making the form of detailed air bubbles forming into each raw material component is well-known so that it may become supersaturation in the flow and pressure requirement of a mixing chamber in the aforementioned foaming machine. It is applying more high-pressure air or N2 gas, for example in 1 each raw material component tank as a concrete method. The method of making the gas in a raw material component a supersaturation state by the mixing chamber etc. is mentioned by decompressing the pressure of the method of dissolving more gas, the method of pouring in gas compulsorily into 2 raw-material transportation piping, and dissolving or distributing, and three mixing chambers below to an ordinary pressure.

[0005] Although these solution gases are extremely few amounts compared with CO2 capacity produced by the reaction of the water and the isocyanate component which are a foaming agent, it is poured in in order to generate more cellular nuclei and to generate detailed air-bubbles form, since fluid pressure declines rapidly by the mixing chamber.

[0006] The gas produced on the other hand by boil of the CO2 gas or the organic solvent generated at the reaction of an isocyanate and water is gas which occurs serially, and in order to carry out only the work which is spread in the cellular nucleus already generated, without making a cellular, almost new nucleus generate, and enlarges the air bubbles, a solution gas differs in work.

[0007] Conventionally, the method of putting a high pressure by the raw material component tank, and forming detailed air bubbles is indicated by JP,61-3663,B (the conventional technology 1), JP,10-58462,A (the conventional technology 2), and JP,59-10915,A.

[0008] (1) In the conventional technology 1, it is reactant mixture. That the fault produced from using the extruding die which consists of the aggregate of the small die which has the die side which is easy to generate the fault and gel by dividing into two or more paths in a center section in flowing into an extruding die should be removed, reactant mixture is made to flow from a single die input, and completing the extruding die which does not make the interior of a die divide or more into two substantially is indicated. However, cellular structure of 100 micrometers or less / KE called microcell cannot be made to generate by several kg tank pressure (pressure of the gas to pour in) shown in the

conventional technology 1.
[0009] (2) these 2 after saturating each component in two airtight containers with gas on the conventional technology 2 component -- mixing -- this mixture -- metal mold -- making it react, changing a pressure and/or temperature inside, and manufacturing foaming synthetic resin is indicated Here, although putting a pressure on an airtight container 60 to 80x102 kPa is indicated and a detailed foam can be realized in this case, while a tankage becomes expensive, in order to fully saturate gas in an airtight container, there is a fault which requires a long time.
[0010] (3) Only pouring in air and N2 gas into transportation piping of a polyol component is indicated by the conventional technology 3. However, this method is general technology currently performed in manufacture of general block form, and it is the limit which is made about (about 150micrometers/(piece)) a maximum of 50% of cellular size by this method to the form which does not pour in gas at most. In addition, although there is also the method of using together the stirrer other than the above-mentioned technology, and making the dissolution quick, this method as well as the conventional technology 3 has a problem in cellular size.
[0011] Moreover, not only an installation cost is expensive, but the method of changing more into a supersaturation state the solution gas in the raw material component which is made to decompress the pressure of a mixing chamber below to an ordinary pressure, and is injected by the mixing chamber has the fault to which cellular size does not become small extremely, either.

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EFFECT OF THE INVENTION

[Effect of the Invention] The manufacture method of detailed air-bubbles form can overly be offered that detailed air-bubbles form can be manufactured continuously for a long time, without also needing a mass tank, without using a reduced pressure mixing chamber facility according to this invention, without the dissolution of gas taking a long time, while not needing a facility of an expensive proof-pressure tank etc., as explained in full detail above. Moreover, while the more flexible form in a soft foam became possible by overly considering as detailed air bubbles, in the rigid foam, the form of low thermal conductivity became possible and manufacture of the form which changes sharply [a property] with capacity in which the same raw material combination is also dissolved was attained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] It aims at the thing which can overly manufacture detailed air-bubbles form continuously for a long time, without also needing a mass tank and for which the manufacture method of detailed air-bubbles form is overly offered, without using a reduced pressure mixing chamber facility, without the dissolution of gas taking a long time, while this invention was not made in consideration of the above-mentioned situation and does not need a facility of an expensive proof-pressure tank etc.

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MEANS

[Means for Solving the Problem] The form manufacturing installation characterized by this invention possessing the following is used. While setting up the raw material component pressure of at least 1 component which is the method of overly manufacturing detailed air-bubbles form, and flows the inside of the aforementioned transportation means more than 20x102kPa (20kg/cm2) it is characterized by dissolving gas in the raw material component in the aforementioned transportation means continuously by the pressure higher than the raw material component pressure which flows the inside of this transportation means -- super- -- the manufacture method of detailed air-bubbles form The pump means of ****** which measures two or more raw material components required to manufacture a polyurethane foam or a polyisocyanurate foam, and is breathed out. Two or more transportation meanses to convey the raw material component breathed out from the aforementioned pump means to the target place. A mixing chamber means to mix two or more of said raw material components.
[0014]
[Embodiments of the Invention] Hereafter, it explains in more detail about this invention.
[0015] In this invention, a raw material component pressure is set as 20x102 or more kPas because the detailed air-bubbles generation effect is small in less than 20x102 kPas. Moreover, as for a raw material component pressure, it is desirable to make it 40x102 or more kPas, and it is still more desirable to make it especially 60x102 or more kPas.
[0016] In this invention, you may pour in continuously the gas injected into a raw material component directly through capillary tubes, such as glass or a metal, inorganic, or an organic open-cell object into the raw material component in piping as a transportation means. By the aforementioned method, although it is difficult, by enlarging distance from pouring to a mixing chamber, and setting up the dissolution time of gas greatly, making it dissolve into a raw material component in large quantities can dissolve a lot of gas into a raw material component, and it can enlarge the detailed air-bubbles effect. Here, as a method of pouring in gas effectively in a raw material component, it is good to make a dynamic mixer or a stood [still] type mixer distribute rather than to only to pour in gas, and to dissolve a lot of gas for a short time into a raw material component. Especially, as a desirable mixer, it is a stood [still] type mixer, and there is no leakage of the fluid from the axis of rotation by the pressure of a high-pressure fluid like a dynamic mixer. Moreover, ultrasonic stirring can be used similarly independently.
[0017] Although there are for example, a screw type and a pin type type as the aforementioned dynamic mixer and there is a method which put the glass bead in the pipe in addition to the screw type which twisted 180 degrees of rectangular boards to the right-and-left opposite direction as the aforementioned stood [still] type mixer, and the pin type type, when a raw material component is a hypoviscosity liquid and a glass-bead method and a raw material component are hyperviscous liquids, a screw type is desirable at the small point of pressure loss.
[0018] In this invention, as gas which injects the inside of a transportation means into the flowing raw material component, although air, N2 gas, argon gas, gaseous helium, CO2 gas, etc. are mentioned, for example, especially CO2 gas is desirable.
[0019] In this invention, in order not to take the method which a high pressure gas is enclosed [method]

with a high-pressure endurance tank over a long time, and dissolves a lot of gas into a raw material component but to dissolve gas for a short time in the transportation means process between a pump means and a mixing chamber means, CO2 gas which is easy to dissolve in a polyurethane-foam raw material or a polyisocyanurate-foam raw material is desirable. Although in the case of CO2 gas a cellular detailed-ized effect is large even if it uses it with 20x102 or more kPas and below critical pressure When it mixes into the raw material component which flows especially by the pressure more than critical pressure at 70x102 or more kPas of a transportation means In the form of kg [25-100]/m3, the diameter of a foam sets in about dozens ofmicrometers/piece, density sets in the form of 300 - 700 kg/m3, and density becomes possible [the thing whose diameter of a foam is about severalmicrometers/piece and for which detailed foam form is overly manufactured].

[0020] by the way, although the technology (latter) of pouring in CO2 gaseous gas into the technology (former) which injects liquefied CO2 into a mixing chamber, and foams to it, or a mixing chamber is in the technology called carbon-dioxide-gas foaming completely apart from this, it should be clearly distinguished from the technology which is this invention CO2 gas which occurs from CO2 of a liquid in the cellular nucleus mainly generated already diffuses the former, using liquefaction CO 2 as a foaming agent, and it grows up a cellular nucleus. Therefore, although a foam does not become small but a foam becomes a little large, it is the technology of manufacturing a low density polyurethane foam or a polyisocyanurate foam, without using a chlorofluocarbon system and a non-chlorofluocarbon system solvent. The latter is technology which is made to distribute CO2 gas uniformly and equalizes the permeability of the whole form rather than work of mainly carrying out differential powder of the CO2 gas by stirring by the mixing chamber, and making the diameter of a foam small.

[0021] By reducing rapidly the pressure of the raw material which is dissolved in large quantities and conveyed by the high-pressure force in a mixing chamber into a raw material component, CO2 gas of this invention is the point that you are going to generate a cellular nucleus in large quantities in an instant, and are going to make it overly form a detailed foam, and is technology completely different from the above-mentioned carbon-dioxide-gas foaming.

[0022] In this invention, although the position which pours in gas is in the raw material component in a raw material transportation means, it is in the middle of piping which specifically connects a mixing chamber to a pump. However, although it is possible to pour in gas in the middle of the portion which carries out a pump action, and the portion which carries out a mixing chamber operation when the pump and the mixing chamber are unifying as a special example, this method is also included in the range of this invention.

[0023] In this invention, although it is used for the general-purpose polyurethane foam as the aforementioned pump means and a gear pump, a bosh pump, etc. are easy to be, in order to send a raw material component to a mixed container by the high-pressure force, a bosh pump is desirable. In the case of a gear pump, the sending pressure of a raw material component is used by about 3x102kPa-60x102kPa, and, in the case of a bosh pump, 30x102kPa-150x102kPa is the use range of a general target.

[0024] Although the mixing chamber used may consist of mere loculus which do not build in the case where the mixer which rotates mechanically is built in, and a mixer in this invention, this does not need to build in a mixer with regards to the size of the pressure of the raw material component injected by the mixing chamber, when it is the raw material pressure which is like [with which the raw material generally injected can be mixed enough].

[0025] Although this invention pours in gas into the raw material component sent from a pump, it is effective to pour into a component with much amount used among two or more components of a polyurethane-foam raw material or a polyisocyanurate-foam raw material generally. That is, even if it pours in into a polyol component or the poly isocyanate component and pours in into minor constituents, such as a foaming agent and a foam stabilizer, there are few effects.

[0026] A special raw material does not need to be used for the polyurethane-foam raw material or polyisocyanurate-foam raw material used for this invention, and it can overly manufacture detailed foam form by in addition to this adding a plasticizer, a bulking agent, a stabilizer, etc. if needed by using a

general-purpose polyol, the poly isocyanate, a foam stabilizer, a catalyst, and a foaming agent as an indispensable component.

[0027] In this invention, generally it is used and a polyether system polyol, a polyester system polyol, a polydien system polyol, and a polycarbonate system polyol are easy to be as a typical kind as a polyol used. The numbers of functional groups are two or more things, and a thing typical as a polyether polyol has a thing, a polyoxy tetramethylene glycol, etc. which carried out the addition polymerization of polyethylene and the polypropylene to the polypropylene glycol, the polyethylene glycol, and the glycerol.

[0028] A thing typical as a polyester polyol has a polyester polyol, a poly lactone polyol, etc. which are made to condense acids, such as low-molecular-weight polyols, such as ethylene glycol and a diethylene glycol, and a dicarboxylic acid, and have an end OH basis.

[0029] In this invention, as a poly isocyanate to be used, generally it is used and an aromatic poly isocyanate, aliphatic isocyanate, and alicycle group isocyanate etc. is mentioned. Especially the desirable poly isocyanate is an aromatic isocyanate, and has 4 and 4' diphenylmethane diisocyanate, a crude polymethylene polyphenylene poly isocyanate, 2, and 4 tolylene diisocyanate and/or 2, and 6 tolylene diisocyanate as a typical thing, for example. Moreover, the denaturation object of these isocyanates, for example, aloha shirt NETO denaturation, buret denaturation, or a cull BOJIMIDO denaturation object is usable similarly.

[0030] In this invention, the foam stabilizer used is easy to be a commercial thing, and surfactants, such as a polysiloxane-polyoxy-alkylene-glycol copolymer or sulfonate-ized castor oil, are used as a typical thing. Moreover, in the case of a polyurethane foam, it is used for the usual urethane foam and organic-metal catalysts, such as the third class amines, such as a triethylenediamine and a morpholine, or stannous octoate, and dibutyltin dilaurate, etc. are easy to be used as a catalyst. Moreover, in the case of a polyisocyanurate foam, after making a NCO/OH index or more into 1.1 generally, generally, a well-known isocyanurate catalyst is usable. For example, quarternary ammonium salt, an organic-acid alkali-metal salt, etc. are used. Potassium acetate, sodium acetate, N, N', N"-tris (3-dimethylamino propyl) hexahydro-s-triazine, etc. are especially specifically common.

[0031] In this invention, low-boiling point liquids, such as water [which reacts with an isocyanate and generates CO2 gas as a foaming agent used], pentane, hexane, cyclohexane, dichloromethane, 1, and 1-dichloro-1-fluoro ethane, can be used.

[0032] In this invention, although it is possible, and a polyol component is lost as a foaming method used by any foaming methods, such as an one-shot process, the prepolymer method, and the KUWAJI prepolymer method, in order to make a polyol and the poly isocyanate especially react beforehand by the prepolymer method and to consider as the prepolymer of an end NCO basis, pouring of gas may be limited to a prepolymer in this case.

[0033] In this invention, all flexible polyurethane foams generally called aforementioned polyurethane foam, half-rigid polyurethane foams, and rigid urethane foams are included. Moreover, with a polyisocyanurate foam, half-hard isocyanurate form and all hard isocyanurate forms are included. Furthermore, when it sees from the field of a manufacturing facility, all well-known manufacture methods, such as a slab form manufacture method, a mould form manufacture method, a spray form manufacture method, a sandwiches form manufacture method, and a RIM foaming method, are contained in the range of this invention.

[Translation done.]

* NOTICES *

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EXAMPLE

[Example] hereafter, one example of this invention is started -- the manufacture method of detailed foam form is overly explained In addition, a numeric value, material, etc. which are stated in the following example do not show an example, and do not specify this invention. First, the equipment which overly manufactures detailed foam form is explained with reference to drawing 1 . **** 1 in drawing shows the poly isocyanate component tank (it is hereafter called the 1st tank) which held the poly isocyanate component 2. N2 chemical cylinder 4 is connected to the upper part of this 1st tank 1 through the N2 gas piping 3. It connects with the mixing chamber 8 through the piping 7 which infixed the bosh high pressure pumping (pump means) 5 and the stood [still] type mixer 6 in the pars basilaris ossis occipitalis of the 1st tank 1 of the above. The aforementioned poly isocyanate component 2 is measured and breathed out by the aforementioned high pressure pumping 5 here, and it is piping.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Explanatory drawing of the equipment concerning this invention used [overly] for the manufacture method of detailed foam form.
[Description of Notations]
1 -- The poly isocyanate component tank (the 1st tank),
2 -- The poly isocyanate component,
3 18 -- N2 gas piping,
4 19 -- N2 chemical cylinder,
5 -- Bosh high pressure pumping (pump means),
6 -- Stood [still] type mixer,
7 16 -- Piping (transportation means),
8 -- Mixing chamber
9 -- Mass-flow meter,
10 -- Carbon-dioxide-gas piping,
11 -- Liquefaction CO2 bomb,
12 -- Stirring motor,
14 -- Mixture
15 -- Polyol component tank (the 2nd tank),
17 -- Gear pump (pump means).

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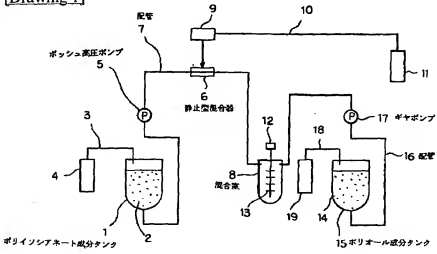
DRAWINGS

[Drawing 1]



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(54)【発明の名称】超微細気泡フォームの製造方法

(57)【要約】
【課題】本発明は、高価な耐圧タンク等の設備を必要とすることないとともに、ガスの溶解に長時間を要することなく、超微細気泡フォームを製造できることを課題とする。
【解決手段】ポリウレタンフォーム又はポリイソシアヌレートフォームを製造するのに必要な複数の原料成分を計量、吐出する複数のポンプ手段と、前記ポンプ手段より吐出される原料成分を目的の場所まで搬送する複数の輸送手段と、前記した複数の原料成分を混合する混合室手段とを具備したフォーム製造装置を用いて、超微細気泡フォームを製造する方法であり、前記輸送手段中を流れる少なくとも１成分の原料成分圧力を２０×１０^{2}ｋＰａ以上に設定するとともに、前記輸送手段中の原料成分に該輸送手段中を流れる原料成分圧力よりも高い圧力にてガスを連続的に溶解させることを特徴とする。

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【特許請求の範囲】

【請求項１】　ポリウレタンフォーム又はポリイソシアヌレートフォームを製造するのに必要な複数の原料成分を計量、吐出する複数のポンプ手段と、前記ポンプ手段より吐出される原料成分を目的の場所まで搬送する複数の輸送手段と、前記した複数の原料成分を混合する混合室手段とを具備したフォーム製造装置を用いて、超微細気泡フォームを製造する方法であり、

前記輸送手段中を流れる少なくとも１成分の原料成分圧力を２０×１０^{2}ｋＰａ以上に設定するとともに、前記輸送手段中の原料成分に脈輸送手段中を流れる原料成分圧力よりも高い圧力にてガスを連続的に溶解させることを特徴とする超微細気泡フォームの製造方法。

【請求項２】　前記輸送手段中を流れる少なくとも１成分の原料成分圧力を４０×１０^{2}ｋＰａ以上に設定することを特徴とする請求項１記載の超微細気泡フォームの製造方法。

【請求項３】　前記輸送手段中を流れる原料成分にガスを溶解させるために静止型ガス溶解器を用いることを特徴とする請求項１あるいは請求項２記載の超微細気泡フォームの製造方法。

【請求項４】　前記ガスがＣＯ$_{2}$ガスであるとともに臨界圧力以上で輸送手段中を流れる原料成分に注入され、かつ少なくとも１成分の原料成分圧力が少なくとも７０×１０^{2}ｋＰａ以上に設定された輸送手段中を流れる原料成分にＣＯ$_{2}$ガス成分を溶解させる請求項１乃至３いずれか記載の超微細気泡フォームの製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、ポリウレタンフォーム又はポリイソシアヌレートフォーム等の超微細気泡フォームを製造する方法に関し、更に詳しくは原料成分の輸送過程において特定条件下にてガスを注入することによって超微細気泡フォームを製造する方法に関する。

【０００２】

【従来の技術】従来、ポリウレタンフォーム又はポリイソシアヌレートフォームは、一般に発泡機と呼ばれる設備を用いて製造されている。この装置は、主として複数のタンクと、複数のポンプと、複数の原料成分を混合する混合室（ミキシングチャンバー）と、前記タンクとポンプを連結する原料輸送配管と、前記ポンプと混合室を連結する輸送配管から構成されている。

【０００３】また、ポリウレタンフォーム又はポリイソシアヌレートフォームは、一般にポリオール、ポリイソシアネート、整泡剤、触媒、発泡剤を必須成分として製造されるのであるが、これらの原料を必要に応じて２以上の成分に分け、前述の発泡機と称される設備にて製造される。この場合、混合すると反応を起こす２以上の成分を分けて複数のタンクに充填し、夫々のタンク、ポンプ手段、輸送手段を経てミキシングチャンバーに射出され、混合される。

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【０００４】ところで、前記発泡機において混合室の圧力条件にて過飽和になるように、各原料成分中にガスを溶解させ微細気泡のフォームを形成させる製造方法は、公知である。具体的な方法としては、例えば

１）各原料成分タンクにおいてより高圧の空気あるいはＮ$_{2}$ガス等をかけることによって、より多くのガスを溶解させる方法、

２）原料輸送配管中に強制的にガスを注入して溶解あるいは分散させる方法、

３）混合室の圧力を常圧以下に減圧することによって、原料成分中のガスを混合室で過飽和状態とする方法、等が挙げられる。

【０００５】これらの溶解ガスは発泡剤である水とイソシアネート成分との反応によって生ずるＣＯ$_{2}$ガス量に比べて極端に少ない量であるが、混合室で流体圧力が急激に低下する為、より多くの気泡核を発生させて微細気泡フォームを生成するために注入される。

【０００６】一方、イソシアネートと水との反応で生成するＣＯ$_{2}$ガスあるいは有機溶剤の沸騰によって生ずるガスは、逐次発生するガスであり、ほとんど新しい気泡核を生成させずに既に生成されている気泡核に拡散してその気泡を大きくする働きのみをするため、溶解ガスとは働きを異にする。

【０００７】従来、原料成分タンクにより高い圧力をかけて微細気泡を形成する方法は、例えば特公昭６１－３６６３号（従来技術１）、特開平１０－５８４６２号（従来技術２）、特開昭５９－１０９１５号に開示されている。

【０００８】（１）従来技術１には、反応性混合物を押し出しダイに流入するに当って、複数個の通路に分けることによる欠点及びゲルを生成しやすいダイ側面を中央部にもつ小ダイの集合体から成る押し出しダイを使用することから生ずる欠点を除去すべく、反応性混合物を単一のダイ流入口から流入させ、ダイ内部を実質的に２以上に分割させない押し出しダイを完成させることが開示されている。しかし、従来技術１に示される数ｋｇタンク圧力（注入するガスの圧力）では、ミクロセルと呼ばれる１００μｍ以下／ケの気泡構造を生成させることはできない。

【０００９】（２）従来技術２には、ガスで二つの密閉容器中にある夫々の成分を飽和させた後、これら２成分を混合し、この混合物を金型内で圧力及び／又は温度を変化させながら反応させて発泡合成樹脂を製造することが開示されている。ここで、圧力は密閉容器に６０～８０×１０^{2}ｋＰａかけることが記載されており、この場合微細気泡を実現できるが、タンク設備が高価になるとともに、密閉容器内に充分にガスを飽和させるために長時間を要する欠点がある。

【００１０】（３）従来技術３には、ポリオール成分の

輸送配管中に空気やN₂ガスを単に注入することが開示されている。しかし、この方法は一般のブロックフォームの製造において行われている一般技術であり、この方法では、せいぜいガスを注入しないフォームに対して最大５０%程度（１５０μm／ケ程度）の気泡サイズにするのが限度である。なお、上記技術の他に、攪拌器を併用して溶解を速くする方法もあるが、この方法も従来技術３と同様、気泡サイズに問題がある。

【００１１】また、混合室の圧力を常圧以下に減圧させて混合室に射出される原料成分中の溶解ガスをより過飽和状態にする方法は、設備費が高価であるばかりでなく、気泡サイズも極端には小さくならない欠点がある。

【００１２】

【発明が解決しようとする課題】本発明は上記事情を考慮してなされたもので、高価な耐圧タンク等の設備を必要とすることがないとともに、ガスの溶解に長時間を要することなく、また減圧混合室設備を使用することもなく、大容量のタンクも必要とせずに長時間連続して超微細気泡フォームを製造し得る超微細気泡フォームの製造方法を提供することを目的とする。

【００１３】

【課題を解決するための手段】本発明は、ポリウレタンフォーム又はポリイソシアヌレートフォームを製造するのに必要な複数の原料成分を計量、吐出する複数のポンプ手段と、前記ポンプ手段より吐出される原料成分を目的の場所まで搬送する複数の輸送手段と、前記した複数の原料成分を混合する混合室手段とを具備したフォーム製造装置を用いて、超微細気泡フォームを製造する方法であり、前記輸送手段中を流れる少なくとも１成分の原料成分圧力を２０×１０² ｋＰａ（２０ｋｇ／ｃｍ²）以上に設定するとともに、前記輸送手段中の原料成分に該輸送手段中を流れる原料成分圧力よりも高い圧力にてガスを連続的に溶解させることを特徴とする超微細気泡フォームの製造方法である。

【００１４】

【発明の実施の形態】以下、本発明について更に詳しく説明する。

【００１５】本発明において、原料成分圧力を２０×１０² ｋＰａ以上に設定するのは、２０×１０² ｋＰａ未満では微細気泡生成効果が小さいからである。また、原料成分圧力は４０×１０² ｋＰａ以上にすることが好ましく、特に６０×１０² ｋＰａ以上にすることが更に好ましい。

【００１６】本発明において、原料成分に注入するガスは、連続的に輸送手段としての配管中の原料成分中にガラスあるいは金属等のキャピラリー、又は無機あるいは有機連続気泡体を通して直接注入してもよい。前記方法では大量に原料成分中に溶解させることは難しいが、注入から混合室までの距離を大きくしてガスの溶解時間を大きく設定することによって大量のガスを原料成分中に溶解させることができ、微細気泡効果を大きくすることができる。ここで、ガスを原料成分中に効果的に注入する方法としては、ガスを単に注入するのではなく、動的混合機あるいは静止型混合器にて分散させ、短時間に大量のガスを原料成分中に溶解させるのが良い。特に好ましい混合器としては静止型混合器であり、動的混合機のような高圧流体の圧力による回転軸からの流体の漏れがない。又、別に超音波攪拌も同様に使用することができる。

【００１７】前記動的混合機としては例えばスクリュー型、ピンタイプ型があり、前記静止型混合器としては例えば長方形の板を左右逆方向に１８０°ひねったスクリュー型、ピンタイプ型以外に、ガラスビーズを管に詰めた方式等があるが、原料成分が低粘度液体の場合にはガラスビーズ方式、原料成分が高粘度液体の場合にはスクリュー型が圧力損失の小さい点で好ましい。

【００１８】本発明において、輸送手段中を流れる原料成分に注入するガスとしては、例えば空気、N₂ガス、アルゴンガス、ヘリウムガス、CO_2ガス等が挙げられるが、特にCO₂ガスが好ましい。

【００１９】本発明においては、高圧耐久性タンクに長時間に渡って高圧ガスを封入して原料成分中に大量のガスを溶解させる方式をとらず、ポンプ手段と混合室手段の間の輸送手段工程において短時間にガスを溶解させるため、ポリウレタンフォーム原料あるいはポリイソシアヌレートフォーム原料に溶解し易いCO₂ガスが好ましい。CO₂ガスの場合、２０×１０² ｋＰａ以上、そして臨界圧以下で使用しても気泡微細化効果は大きいが、特に臨界圧以上の圧力で輸送手段中の７０×１０² ｋＰａ以上で流れる原料成分中に混入した場合には、密度が２５～１００ｋｇ／m³のフォームにおいては気泡径が数十μm／ケ程度、密度が３００～７００ｋｇ／m³のフォームにおいては気泡径が数μm／ケ程度の超微細気泡フォームを製造することが可能となる。

【００２０】ところで、これとは全く別に炭酸ガス発泡と呼ばれる技術のなかに、液状のCO₂を混合室に注入して発泡する技術（前者）あるいは混合室の中に気体のCO₂ガスを注入する技術（後者）があるが、本発明の技術とはっきりと区別されるべきである。前者は、液化CO₂を発泡剤として用いて、主に既に生成している気泡核に液体のCO₂から発生するCO₂ガスが拡散して、気泡核を成長させる。従って、気泡はかさくなるのではなく、気泡は少々大きくなるが、フロン系、非フロン系溶剤を使用せずに低密度ポリウレタンフォームあるいはポリイソシアヌレートフォームを製造する技術である。後者は、主にCO₂ガスを混合室での撹拌により微分散させるものであり、気泡径を小さくするという働きよりもCO₂ガスを均一に分散させ、フォーム全体の通気度を均一化する技術である。

【００２１】本発明のCO₂ガスは原料成分中に大量に

溶解させておき、混合室にて高圧力で輸送されてくる原料の圧力を急激に低下させることにより、瞬時に気泡核を大量に発生させて超微細気泡を形成させようとする点で、前述の炭酸ガス発泡とは全く別の技術である。

【００２２】本発明において、ガスを注入する位置は原料輸送手段中の原料成分の中であるが、具体的にはポンプと混合室を結ぶ配管途中である。しかし、特殊な例としてポンプと混合室とが一体化している場合には、ポンプ作用する部分と混合室作用をする部分との中間にガスを注入することが考えられるが、本方法も本発明の範囲に含まれる。

【００２３】本発明において、前記ポンプ手段としては、汎用のポリウレタンフォームに使用されているものでよく、ギヤポンプ、ポッシュポンプ等があるが、高圧力で原料成分を混合容器に送るためポッシュポンプが好ましい。ギヤポンプの場合には、原料成分の送付圧力は３×１０^{2}ｋＰａ～６０×１０^{2}ｋＰａ程度で使用され、ポッシュポンプの場合は、３０×１０^{2}ｋＰａ～１５０×１０^{2}ｋＰａが一般的の使用範囲である。

【００２４】本発明において、使用される混合室は機械的に回転するミキサーを内蔵する場合とミキサーを内蔵しない単なる室からなる場合とがあるが、これは混合室に射出される原料成分の圧力の大きさに関係し、一般的に射出される原料が十分混合できる程の原料圧力の場合にはミキサーを内蔵しなくても良い。

【００２５】本発明は、ポンプより送られる原料成分中にガスを注入するのであるが、一般的にはポリウレタンフォーム原料あるいはポリイソシアヌレートフォーム原料の複数成分の内、使用量の多い成分に注入するのが効果的である。即ち、ポリオール成分あるいはポリイソシアネート成分中に注入するのであり、発泡剤や整泡剤等の微量成分中に注入しても効果は少ない。

【００２６】本発明に使用するポリウレタンフォーム原料あるいはポリイソシアヌレートフォーム原料は、特殊な原料を使用する必要はなく、汎用のポリオール、ポリイソシアネート、整泡剤、触媒及び発泡剤を必須成分としてその他、可塑剤、充填剤、安定剤などを必要に応じて添加することによって超微細気泡フォームを製造することができる。

【００２７】本発明において、使用されるポリオールとしては、一般に使用されるもので良く、代表的種類としてはポリエーテル系ポリオール、ポリエステル系ポリオール、ポリジエン系ポリオール、ポリカーボネート系ポリオールがある。ポリエーテルポリオールとして代表的なものは、官能基数が２以上のものであり、ポリプロピレングリコール、ポリエチレングリコール、グリセリンにポリエチレン、ポリプロピレンを付加重合させたもの、ポリオキシテトラメチレングリコール等がある。

【００２８】ポリエステルポリオールとして代表的なものは、エチレングリコール、ジエチレングリコール等の低分子量ポリオールとジカルボン酸等の酸を縮合させて末端ＯＨ基を有するポリエステルポリオール、ポリラクトンポリオール等がある。

【００２９】本発明において、使用するポリイソシアネートとしては、一般に使用されるものであり、芳香族ポリイソシアネート、脂肪族イソシアネート、脂環族イソシアネート等が挙げられる。特に好ましいポリイソシアネートは芳香族イソシアネートであり、代表的なものとしては、例えば４，４’ジフェニルメタンジイソシアネート、粗製ポリメチレンポリフェニレンポリイソシアネート、２，４トリレンジイソシアネート及び／又は２，６トリレンジイソシアネートがある。また、これらイソシアネートの変性体、例えばアロハネート変性、ビューレット変性あるいはカルボジミド変性体等も同様に使用可能である。

【００３０】本発明において、使用される整泡剤は市販ものでよく、代表的なものとしては、ポリシロキサンーポリオキシアルキレングリコール共重合体あるいはスルホネート化ヒマシ油等の界面活性剤が使用される。また、触媒としては、ポリウレタンフォームの場合には、通常のウレタンフォームに使用されているものでよく、例えばトリエチレンジアミン、モルホリン等の三級アミン類あるいはスタナスオクトエート、ジブチルチンジラウレート等の有機金属触媒等が使用される。また、ポリイソシアヌレートフォームの場合には、一般的にＮＣＯ／ＯＨインデックスを１．１以上とした上で一般に公知なイソシアヌレート触媒が使用可能である。例えば、４級アンモニウム塩、有機酸アルカリ金属塩等が使用される。具体的には、酢酸カリウム、酢酸ナトリウム、Ｎ，Ｎ’，Ｎ”－トリス（３－ジメチルアミノプロピル）ヘキサヒドロ－ｓ－トリアジン等が特に一般的である。

【００３１】本発明において、使用される発泡剤としては、イソシアネートと反応してＣＯ$_{2}$ガスを生成する水やベンタン、ヘキサン、シクロヘキサン、ジクロロメタン、１，１－ジクロロ－１－フルオロエタン等の低沸点液体を使用することができる。

【００３２】本発明において、使用される発泡方式としては、ワンショット法、プレポリマー法、クワジプレポリマー法等のいかなる発泡方式でも可能であり、特にプレポリマー法ではポリオールとポリイソシアネートとを前もって反応させて末端ＮＣＯ基のプレポリマーとする為、ポリオール成分がなくなるが、この場合ガスの注入はプレポリマーに限定される場合がある。

【００３３】本発明において、前記ポリウレタンフォームとは、一般に云う軟質ポリウレタンフォーム、半硬質ポリウレタンフォーム及び硬質ウレタンフォーム全てを含む。また、ポリイソシアヌレートフォームとは、半硬質イソシアヌレートフォーム、硬質イソシアヌレートフォーム全てを含む。更に、製造設備の面から見ると、スラブフォーム製造方式、モールドフォーム製造方式、ス

プレーフォーム製造方式、サンドイッチフォーム製造方式、ＲＩＭ発泡方式等公知の製造方式全てが本発明の範囲に含まれる。

【００３４】

【実施例】以下、本発明の一実施例に係る超微細気泡フォームの製造方法について説明する。なお、下記実施例で述べる数値、材料等は一例を示すもので、本発明を特定するものではない。まず、超微細気泡フォームを製造する装置について図１を参照して説明する。図中の符番１は、ポリイソシアネート成分２を収容したポリイソシアネート成分タンク（以下、第１のタンクと呼ぶ）を示す。この第１のタンク１の上部には、N_2ガス配管３を介してN_2ガスボンベ４が接続されている。前記第１のタンク１の底部には、ポッシュ高圧ポンプ（ポンプ手段）５及び静止型混合器６を介装した配管７を介して混合室８に接続されている。ここで、前記高圧ポンプ５により前記ポリイソシアネート成分２が計量，吐出され、配管（輸送手段）７を経て前記混合室８に吐出される。

【００３５】前記静止型混合器６には流量コントロール付きマスフロメータ９を介装した炭酸ガス配管１０を介して液化CO_2ボンベ１１が接続されている。この液化CO_2ボンベ１１よりCO_2ガスが炭酸ガス配管１０を通ってマスフロメータ９より静止型混合器６にCO_2ガスが注入され、CO_2ガスが原料成分に拡散溶解される。前記混合室８内には、撹拌モータ１２により回転する回転羽根１３が配置されている。ここで、前記混合室８と撹拌モータ１２と回転羽根１３とにより混合室手段が構成されている。

【００３６】前記混合室８には、ポリオール成分の他、整泡剤，触媒、発泡剤を適宜配合した混合物１４を収容したポリオール成分タンク（以下、第２のタンクと呼ぶ）１５が配管１６を介して接続されている。ここで、前記配管１６には、ギヤポンプ（ポンプ手段）１７が介装されている。このギヤポンプ１７によりポリオール成分が計量、吐出され、配管１６を介して前記混合室８に射出され、混合室８より吐出されてポリイソシアネートと反応してフォームとなる。また、前記第２のタンク１５の上部には、N_2ガス配管１８を介してN_2ガスボンベ１９が接続されている。

【００３７】次に、こうした構成の装置を用いて超微細気泡フォームを製造する場合について説明する。前記混合室８には、第１のタンク１から配管７を経てポリイソシアネート成分２を送るとともに、第２のタンク１５からポリオール成分１４を配管１６を経て送る。この際、前記配管７にはポッシュ高圧ポンプ５を介装して、配管７を流れるポリイソシアネート成分２の圧力を50×10^2ｋＰａ以上に設定するとともに、配管７に静止型混合器６を介装して、イソシアネート成分の圧力よりも高圧の60×10^2ｋＰａで大量のCO_2ガスを短時間に溶解させる。一方、前記配管１６にはギヤポンプ１７を介装して、配管１６を流れるポリオール成分１４の圧力を10×10^2ｋＰａ以上に設定している。

【００３８】このように、上記実施例では、輸送手段としての配管７中を流れるポリイソシアネート成分２の圧力をポッシュ高圧ポンプ５により高くするとともに、液化CO_2ボンベ１１から配管７中のポリイソシアネート成分２にCO_2ガスを大量に注入して溶解させ、混合室８にて急減に常圧まで減圧することにより、より多くの気泡核を発生させ、数μｍ／ケ～数十μｍ／ケ程度の超微細気泡フォームを形成することができる。特に、配管７中を流れる原料圧力を高め、臨界圧力のガスで注入することによって非常に短時間に注入したガスを溶解することができ、更に静止型混合器６を併用することによって更により短時間に大量のガスを原料成分に溶解でき、結果として超微細な気泡フォームを製造することができる。

【００３９】

【発明の効果】以上詳述した如く本発明によれば、高価な耐圧タンク等の設備を必要とすることがないとともに、ガスの溶解に長時間を要することなく、また減圧混合室設備を使用することもなく、大容量のタンクも必要とせずに長時間連続して微細気泡フォームを製造し得る超微細気泡フォームの製造方法を提供できる。また、超微細気泡とすることによって、軟質フォームではより柔軟なフォームが可能となると共に、硬質フォームでは低熱伝導率のフォームが可能となり、同一原料配合でも溶解させるガス量により特性の大幅に異なるフォームの製造が可能となった。

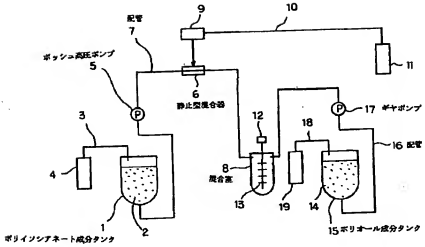
【図面の簡単な説明】

【図１】本発明に係る超微細気泡フォームの製造方法に使用される装置の説明図。

【符号の説明】

１…ポリイソシアネート成分タンク（第１のタンク）、
２…ポリイソシアネート成分、
３，１８…N_2ガス配管、
４，１９…N_2ガスボンベ、
５…ポッシュ高圧ポンプ（ポンプ手段）、
６…静止型混合器、
７，１６…配管（輸送手段）、
８…混合室、
９…マスフロメーター、
１０…炭酸ガス配管、
１１…液化CO_2ボンベ、
１２…撹拌モータ、
１４…混合物、
１５…ポリオール成分タンク（第２のタンク）、
１７…ギヤポンプ（ポンプ手段）。

【図１】



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